

[German Patent No. 257 740 A3]

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A METHOD FOR PRODUCING C<sub>2</sub> TO C<sub>4</sub> OLEFINS

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Abstract

Alcohol mixtures that contain methanol and higher aliphatic alcohols are obtained by reacting gases that contain essentially carbon monoxide and hydrogen, for example, synthesis gas, on copper-containing catalysts. Their conversion on zeolite catalysts takes place at elevated temperatures and pressures over 100 kPa. In accordance with the invention a weight ratio of methanol to higher alcohols of 0.6-5.6, preferably 0.6-1.5, is established in the alcohol mixture and then the conversion is carried out.

Claims

1. A method for producing C<sub>2</sub>-C<sub>4</sub> olefins by reacting carbon monoxide and hydrogen-containing gases, for example, synthesis gas, on copper-containing catalysts to form an alcohol mixture that contains methanol and higher aliphatic alcohols and converting the higher aliphatic

alcohols on zeolite catalysts with pentasil structure at temperatures of 250-600°C and pressures over 100 kPa, which is characterized by the fact that in the alcohol mixture a weight ratio of methanol to higher alcohols of 0.6-5.6 is established.

2. A method as in Claim 1, which is characterized by the fact that a weight ratio of methanol to higher alcohols of 0.6-1.5 is established.

#### Field of invention

The invention concerns a method for producing C<sub>2</sub>-C<sub>4</sub> olefins from alcohol mixtures that were produced from carbon monoxide and hydrogen-containing gases.

#### Prior art

Generating an alcohol mixture containing methanol and higher alcohols from carbon monoxide and hydrogen-containing gases like synthesis gas using copper-containing catalysts, separating the methanol from this alcohol mixture and dehydrating the higher aliphatic alcohols, in particular ethanol and propanol, on a dehydration catalyst to form the corresponding olefins is already known (DE-AS 3 005 550). This method has the disadvantage of high energy cost, since the methanol must be completely separated from the alcohol mixture before the alcohol dehydration and all of the energy for the endothermic dehydration of the higher alcohols must be externally supplied. There is, moreover, the disadvantage that the methanol fractions of the original alcohol mixture are not used for olefin formation.

On the other hand, converting alcohol mixtures to olefin-containing hydrocarbons on zeolite catalysts is known. Various means are employed to remove the heat of reaction that is produced.

Thus, conducting the conversion of lower alcohols, ethers, also in mixtures with other compounds like higher alcohols or carbonyl compounds, so that in a first step methanol is converted to a dimethyl ether-methanol-water mixture while releasing the first part of the heat of reaction, the intermediate product is indirectly cooled and then further reacted to form a hydrocarbon mixture with indirect cooling of the second catalyst zone is known (US 4 052 479). This method has the disadvantage that it operates only at a maximum 25% conversion of the feedstock and with high methanol recycling.

Furthermore, conducting the conversion of lower alcohols in a fluidized bed reactor and removing the heat of reaction by cooling the catalyst in special cooling zones by stripping with steam, light gases (optionally separated from the reaction products) and indirectly via coolers is known (EP 15715). Furthermore, removing the heat of reaction of the conversion of methanol, C<sub>2</sub>-C<sub>3</sub> alcohols, their ether derivatives or mixtures of oxygenates from synthesis gas, oxygenates from Fischer-Tropsch synthesis by catalyst and product cooling indirectly using organic oils or

salt melts is known (EP 108 482). Also, the heat of reaction in the conversion of  $C_1$ - $C_3$  monoalcohols, their mixtures and mixtures of one or more such alcohols and similar oxygenates and/or oxygenates from Fischer-Tropsch synthesis is likewise removed by catalyst cooling via equipment facilities (EP 99 690).

Furthermore, converting alcohols, their ether derivatives, synthetic oxygen compounds, including oxygen compounds from Fischer-Tropsch synthesis, so that the heat of reaction is withdrawn via a plurality of heat exchanger tubes in a fluidized bed or reaction zone is known (DE 3 040 957). All of the said methods have the disadvantage that the removal of heat takes place only by indirect cooling with the corresponding heat losses and considerable industrial cost for the cooling devices.

Furthermore, supporting the removal of heat in the conversion of alcohols and/or ethers with no more than 4 C atoms, in addition to a methanol circulation, by adding inert diluents like steam, nitrogen, hydrogen, carbon dioxide and paraffins is known (DE 2 615 150). However, this method has the disadvantage that the added diluents must be again removed in the further processing of the product.

All of the said methods have the disadvantage that the heat produced in the conversion of the oxygen-containing compounds is not utilized directly for chemical reactions, but rather is transported away.

A method for producing lower olefins, principally ethylene, monoaromatic compounds and carburetor fuels by catalytic conversion of methanol (or mixtures of oxygen-containing organic compounds) and hydrocarbons, including those in the gasoline and gas oil boiling range, in ratios of 10:1 to 1:5 on high-silica-containing zeolite catalysts at temperatures from 600-800°C, through which these disadvantages are supposed to be alleviated, is described in DE 3 437 698. Coupling the exothermic methanol conversion to the endothermic decomposition of the hydrocarbons does lead to better control of the exothermy, but the method has the disadvantage of an additional product economy for the hydrocarbons that are additionally to be supplied for methanol conversion.

#### Goal of invention

The goal of the invention is to improve the economy of methods for producing  $C_2$ - $C_4$  olefins from alcohol mixtures.

#### Nature of invention

There was thus the task of developing a method for producing  $C_2$ - $C_4$  olefins from alcohol mixtures in which the technological cost for the overall process is reduced. This task is solved in accordance with the invention by the fact that, through the conversion of carbon monoxide and

hydrogen-containing gases, for example, synthesis gas, on copper-containing catalysts to form an alcohol mixture that contains methanol and higher aliphatic alcohols, and conversion of the higher aliphatic alcohols on zeolite catalysts of pentasil type at temperatures from 250-600°C and at pressures over 100 kPa, a weight ratio of methanol to higher alcohols from 0.6-5.6 is established in the alcohol mixture. Preferably a weight ratio of methanol to higher alcohols from 0.6-1.5 is established. The simultaneous presence of varying amounts of water in the input product does not have a troublesome effect either on the synthesis of olefins or on the subsequently required separation processes. It follows from this that for the said synthesis of the alcohol mixture there is no need for removal of CO<sub>2</sub> from the circulating gas synthesis or there is a need only for limited removal that can be carried out with traditional means.

With the establishment of the weight ratio between methanol and higher alcohols in accordance with the invention, the conversion of the alcohol mixture on the conversion catalyst achieves largely a heat equilibrium between the exothermic methanol conversion and the endothermic dehydration of the higher alcohols that leads to a nearly thermoneutral reaction. With that the energy for the alcohol dehydration is produced by the methanol conversion while at the same time additional olefin formation is produced.

The establishment of the specific weight ratio of methanol to higher alcohols preferably takes place by distilling out a part of the methanol from the alcohol mixture obtained in the alcohol synthesis, but it also can take place so that the alcohol synthesis is carried out under conditions that lead to such a mixture, or so that C<sub>2+</sub> alcohols that were obtained by other processes are added. The methanol obtained by distilling methanol out can be returned to the alcohol synthesis. Zeolites of pentasil type, for example, ones based on zeolite LZ40 (see DD Patent 219 639) or heteropolyacid-containing catalysts are suitable as conversion catalysts. These catalysts can be used in a mixture with dehydration catalysts, for example, aluminum oxide. The conversion takes place at a pressure of 100 kPa and higher, preferably at 200-1000 kPa. The catalyst load [hourly space velocity] of organic product is 0.3-5.0 L/L of catalyst per hour, preferably 0.5-1.5 L/L of catalyst h. The process can be carried out in the presence of an inert gas, such as hydrocarbons or carbon dioxide. Complete alcohol conversion is achieved. The conversion is carried out in a fixed or fluidized bed. The alcohol mixtures that are used for conversion contain, besides methanol, C<sub>2</sub>-C<sub>10</sub> normal alcohols and isoalcohols as well as ethers, esters, carbonyl compounds and optionally hydrocarbons in amounts of <5 wt% each. The alcohol mixtures can have a water content up to 80 wt%. However, the method is also suitable for alcohol mixtures from which water has been removed.

The reaction product is cooled to temperatures under 131 K. The product is separated in a separator into a lower aqueous phase, an upper hydrocarbon phase and a gas phase. The aqueous phase is discarded as process wastewater. It no longer contains any alcohol. Methane and the C<sub>2</sub>-

C<sub>4</sub> olefins are separated from the gas phase in the usual way after carbon dioxide separation. The remaining components of the gas phase and the C<sub>5+</sub> hydrocarbons of the liquid phase can be recycled to the conversion reactor or sent to an additional reactor for thermal cleavage to olefins.

## Embodiment examples

### Example 1

320 g methanol was distilled out of 1000 g of an alcohol mixture that was obtained by the reaction of carbon monoxide and hydrogen on a copper-containing catalyst and contained, in wt% of the liquid fractions, 53% methanol, 17% ethanol, 7% propanols, 3.5% butanols, 1.0% higher alcohols, 0.5% hydrocarbons, 18% water. The remaining alcohol mixture had a weight ratio of methanol to higher alcohols of 0.74. The water-containing mixture obtained after distilling out a part of the methanol was reacted at 250°C, a pressure of 200 kPa and a catalyst load of 0.8 mL (with respect to oxygen-containing organic product components) per mL of catalyst per hour on a catalyst consisting of 70 wt% zeolite with pentasil structure (LZ 40) that contained 2.6 wt% magnesium and 30 wt% aluminum oxide. The reaction product consisted of, with respect to input CH<sub>2</sub>, 28.5% ethene, 20.4% propene, 11.9% butanes, 37.7% C<sub>4</sub><sup>+</sup> hydrocarbons and 1.5% C<sub>1</sub>-C<sub>3</sub> paraffins. The alcohol conversion was 100%.

### Example 2

1000 g of an alcohol mixture that was obtained by reacting carbon monoxide and hydrogen on a copper-containing catalyst and that contained, in wt% of the liquid fractions, 82.0% methanol, 8.1% ethanol, 4.1% propanols, 4.3% butanols, 1.4% higher alcohols, 0.1% hydrocarbons (where the weight ratio of methanol to higher alcohols was 4.58), was reacted at 370°C, a pressure of 200 kPa and a catalyst load of 1.5 mL (with respect to oxygen-containing organic product components) per mL of catalyst per hour on a catalyst consisting of 80 wt% zeolite with pentasil structure (HS 30) and 20 wt% boehmite. The reaction product consisted, with respect to input CH<sub>2</sub>, of 20.2% ethene, 34.2% propene, 19.6% butanes, 24.3% C<sub>4</sub><sup>+</sup> hydrocarbons (less butanes) and 1.7% C<sub>1</sub>-C<sub>3</sub> paraffins. The alcohol conversion was complete.

### Example 3

1000 g of an alcohol mixture that was obtained by reacting carbon monoxide and hydrogen on a copper-containing catalyst and that contained, in wt% of the liquid fractions, 84.5% methanol, 6.7% ethanol, 3.9% propanols, 3.4% butanols, 1.1% higher alcohols, 0.4% hydrocarbons (where the weight ratio of methanol to higher alcohols was 5.6), was reacted at 350°C, a pressure of 200 kPa and a catalyst load of 1.1 mL (with respect to oxygen-containing

organic product components) per mL of catalyst per hour on a catalyst consisting of 65 wt% zeolite with pentasil structure (LZ 40) and 35 wt% boehmite. The reaction product consisted, with respect to input  $\text{CH}_2$ , of 24.3% ethene, 27.7% propene, 18.4% butanes, 28.0%  $\text{C}_4^+$  hydrocarbons (less butanes) and 1.6%  $\text{C}_1\text{-C}_3$  paraffins. The alcohol conversion was complete.